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Analytical Solutions for Sequentially Reactive Transport with Different Retardation Factors

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Abstract

Integral transforms have been widely used for deriving analytical solutions for solute transport systems. Often, analytical solutions can only be written in closed form in frequency domains and numerical inverse-transforms have to be involved to obtain semi-analytical solutions in the time domain. For this reason, previously published closed form solutions are restricted either to a small number of species or to the same retardation assumption. In this paper, we applied the solution scheme proposed by Bauer *et al.* [2001] in the time domain. Using available analytical solutions of a single species transport with first-order decay without coupling with its parent species concentration as fundamental solutions, a daughter species concentration can be expressed as a linear function of those fundamental solutions. The implementation of the solution scheme is straight forward and exact analytical solutions are derived for one- and three-dimensional transport systems.

Key words: *Analytical solution, retardation factor, multispecies reactive transport, first-order reaction.*

1. Introduction

The analytical solution of Sun *et al.* [1999] to sequentially reactive transport has been used as a screening tool for evaluating groundwater contamination and simulating natural attenuation [Aziz *et al.*, 1999]. However, the solution is limited to cases where retardation factors of all species are equal. There is a need to develop analytical solutions to the system with different retardation factors to accurately simulate natural conditions.

Derivation of analytical solutions of solute transport system usually involves complex mathematical manipulation in order to convert solutions from a frequency domain to a time domain. For this reason, previously published analytical solutions to the transport of first-order decay chains are limited to a small number of species [van Genuchten, 1985; Lunn *et al.*, 1996]. Although Sun *et al.* [1999] extended analytical solutions to N-species, retardation factors were not incorporated. Eykholt and Li [2000] developed a semi-analytical solution of a linear reaction network using a response function approach. Since numerical convolution is involved, it is difficult to implement the approach as a screening tool. Recently, Bauer *et al.* [2001] developed a Laplace domain solution using a recursive form. The concentration of a daughter species is expressed as a linear function of ancestor concentrations and the factor of each species concentration is calculated using the recursive form. Though Bauer *et al.* [2001] has made significant progress in first-order reactive transport, the complexity of inverse Laplace transform makes the code implementation difficult. When numerical inverse Laplace transforms are involved, the approach becomes even more complicated. Both Eykholt and Li [2000] and Bauer *et al.* [2001] are based on the unimolar assumption, that is, the stoichiometry of the reaction is such that 1 mol of product is produced by consuming 1 mol of reactant.

In order to avoid the difficulty with inverse Laplace transforms and with numerical processes, we propose an approach to develop closed form solutions of first-order reactive chains in the time domain. We also incorporate yield coefficient factors to the solution approach and analytical solutions. For the sake of simplicity, we demonstrate the solution scheme for a one-dimensional solution to a four-species reactive problem. The solution derived in this paper is compared with Lunn *et al.* [1996] and Sun *et al.* [1999]. Further, we extended the one-dimensional solutions to a three-dimensional system.

2. First-order reactive transport

The transport of a first-order decay chain can be written as [Bear, 1979]:

$$\mathcal{L}(c_i) = R_i \frac{\partial c_i}{\partial t} + R_i k_i c_i - R_{i-1} y_{i-1} k_{i-1} c_{i-1}, \quad \forall i = 1, 2, ..., n, \tag{1}$$

where $\mathcal{L}$ is the advective-dispersive operator, which is linear in c_i and can be simplified in a homogenous one-dimensional column as

$$\mathcal{L} = D \frac{\partial^2}{\partial x^2} - v \frac{\partial}{\partial x} \tag{2}$$

where v is the constant flow velocity $[LT^{-1}]$ and D represents a constant hydrodynamic dispersion coefficient $[L^2T^{-1}]$:

$$D = av + \mathcal{D} \tag{3}$$

where a is dispersivity $[L]$, $\mathcal{D}$ is the molecular diffusion coefficient $[L^2T^{-1}]$, and R_i and k_i represent the retardation factor and the first-order decay rate of species i, respectively. y_{i-1} is the stoichiometrical yield factor calculated as the concentration ratio of c_i to c_{i-1} in the reaction from species $i-1$ to species i. Eq. (1) differs from the basic equation of Sun *et al.* [1999] by the species-specific retardation factors. The transform of Sun *et al.* [1999] fails to derive analytical solutions when $R_i \neq R_j$. $\mathcal{D}$ is assumed to be negligible, thus, $D = av$ is used in the rest of this paper.

3. Solution method

Since equation (1) for species i is linear in c_i, the solution of c_i can be written as a linear combination of the fundamental solutions $\Omega_j \quad \forall j = 1, 2, \cdots, n$

$$c_i = \sum_{j=1}^{i} A_j^i \Omega_j, \tag{4}$$

or in matrix format

$$\mathbf{c} = \mathbf{A\Omega}, \tag{5}$$

where Ω_i, $\forall i = 1, \cdots, n$, represents the analytical solution of ith species concentration in the time domain without coupling with the concentration of its parent species, c_{i-1},

$$\mathcal{L}(\Omega_i) = R_i \frac{\partial \Omega_i}{\partial t} + R_i k_i \Omega_i, \quad \forall i = 1, 2, ..., n. \tag{6}$$

$\mathbf{A}$ is called transform matrix and $A_j^i = 0 \; \forall j > i$. If all components of $\mathbf{A}$, $A_j^i, \forall j < i, i = 1, 2, \cdots, n$, can be expressed as closed form functions of system parameters and fundamental solutions, $\Omega_j, j = 1, 2, \cdots, i$, the analytical solutions of $\mathbf{c}$ in (5) become available.

Similarly to Bauer *et al.* [2001], by substituting (4) into (1),

$$\sum_{j=1}^{i} A_j^i \left[(R_i - R_j) \frac{\partial \Omega_j}{\partial t} + (R_i k_i - R_j k_j) \Omega_j \right] = \sum_{j=1}^{i-1} A_j^{i-1} R_{i-1} y_{i-1} k_{i-1} \Omega_j. \tag{7}$$

Since the last term on the left hand of equation (7) equals zero when $j = i$,

$$\sum_{j=1}^{i-1} A_j^i \left[(R_i - R_j) \frac{\partial \Omega_j}{\partial t} + (R_i k_i - R_j k_j) \Omega_j \right] = \sum_{j=1}^{i-1} A_j^{i-1} R_{i-1} y_{i-1} k_{i-1} \Omega_j. \tag{8}$$

Equation (8) holds, if each term on the left equals the corresponding term on the right,

$$A_j^i \left[(R_i - R_j) \frac{\partial \Omega_j}{\partial t} + (R_i k_i - R_j k_j) \Omega_j \right] = A_j^{i-1} R_{i-1} y_{i-1} k_{i-1} \Omega_j \quad \forall j = 1, 2, \cdots, i-1. \tag{9}$$

Then, the components of the transform matrix can be written in a recursive format

$$A_j^i = A_j^{i-1} \frac{R_{i-1} y_{i-1} k_{i-1} \Omega_j}{(R_i - R_j) \frac{\partial \Omega_j}{\partial t} + (R_i k_i - R_j k_j) \Omega_j}. \tag{10}$$

If $R_i = R_j$,

$$A_j^i = A_j^{i-1} \frac{y_{i-1} k_{i-1}}{k_i - k_j}, \tag{11}$$

the transform format of Sun *et al.* [1999] can be derived. Therefore, the approach Sun *et al.* [1999] proposed is a typical case of (10).

4. Solution Implementation

The analytical solution of Bear [1979, p. 268] to a single species transport with first-order decay in a semi-infinite column is written as:

$$f = \frac{c_o}{2} \mathbf{exp}(\alpha x) \mathbf{erfc}(\beta) \tag{12}$$

where

$$\alpha = \frac{1}{2a} - \left(\frac{1}{4a^2} + \frac{k}{D} \right)^{1/2} \qquad \beta = \frac{x - \left(v^2 + 4kD\right)^{1/2} t}{2\,(Dt)^{1/2}} \qquad D = av.$$

Let

$$\Omega_i = \frac{1}{2} \mathbf{exp}(\alpha_i x) \mathbf{erfc}(\beta_i) \quad \forall i = 1, 2, \cdots, n. \tag{13}$$

Correspondingly,

$$\alpha_i = \frac{1}{2a} - \left(\frac{1}{4a^2} + \frac{k_i}{D_i} \right)^{1/2} \quad \beta_i = \frac{x - \left(v_i^2 + 4k_i D_i\right)^{1/2} t}{2\,(D_i t)^{1/2}} \quad D_i = a v_i$$

where $v_i = v/R_i$ is the transport velocity of species i. When $x = 0$,

$$\Omega_i|_{x=0} = 1, \quad \forall i = 1, 2, \cdots, n. \tag{14}$$

When $\beta \gg 2$, Ω function reaches steady state

$$\Omega_i = \mathbf{exp}(\alpha_i x) \quad \forall \beta_i \gg 2, \quad i = 1, 2, \cdots, n. \tag{15}$$

Then, the first derivative of Ω_i in terms of time can be written as

$$\frac{\partial \Omega_i}{\partial t} = \frac{1}{4\sqrt{D_i \pi}} \mathbf{exp}\left(\alpha_i x - \beta_i^2\right) \left[\frac{x}{t^{3/2}} + \sqrt{\frac{v_i^2 + 4k_i D_i}{t}}\right] \quad \forall i = 1, 2, \cdots, n. \tag{16}$$

To implement this solution scheme, we take a transport of four sequentially reactive species as an example. According to (4),

$$\left\{\begin{array}{lllll} c_1 & = & A_1^1\Omega_1 & & \\ c_2 & = & A_1^2\Omega_1 & +A_2^2\Omega_2 & \\ c_3 & = & A_1^3\Omega_1 & +A_2^3\Omega_2 & +A_3^3\Omega_3 \\ c_4 & = & A_1^4\Omega_1 & +A_2^4\Omega_2 & +A_3^4\Omega_3 \quad +A_4^4\Omega_4. \end{array}\right. \tag{17}$$

If the boundary condition is defined as

$$\left\{\begin{array}{lllllll} c_1|_{x=0} & = & A_1^1\Omega_1 & & & & = c_1^o \\ c_2|_{x=0} & = & A_1^2\Omega_1 & +A_2^2\Omega_2 & & & = c_2^o \\ c_3|_{x=0} & = & A_1^3\Omega_1 & +A_2^3\Omega_2 & +A_3^3\Omega_3 & & = c_3^o \\ c_4|_{x=0} & = & A_1^4\Omega_1 & +A_2^4\Omega_2 & +A_3^4\Omega_3 & +A_4^4\Omega_4 & = c_4^o \end{array}\right. \tag{18}$$

the components of the transform matrix $\mathbf{A}$ can be derived successively as

$$\left\{\begin{array}{lllll} A_1^1 & & & & = c_1^o \\ \downarrow & & & & \\ A_1^2 & +A_2^2 & & & = c_2^o \\ \downarrow & \downarrow & & & \\ A_1^3 & +A_2^3 & +A_3^3 & & = c_3^o \\ \downarrow & \downarrow & \downarrow & & \\ A_1^4 & +A_2^4 & +A_3^4 & +A_4^4 & = c_4^o \end{array}\right. \quad \left\{\begin{array}{llllll} A_1^1 = & c_1^o & & & \\ & & & & \\ A_2^2 = & c_2^o & -A_1^2 & & \\ & & & & \\ A_3^3 = & c_3^o & -A_1^3 & -A_2^3 & \\ & & & & \\ A_4^4 = & c_4^o & -A_1^4 & -A_2^4 & -A_3^4 \end{array}\right. \tag{19}$$

$$A_1^2 = A_1^1 \frac{R_1 y_1 k_1 \Omega_1}{(R_2 - R_1)\frac{\partial \Omega_1}{\partial t} + (R_2 k_2 - R_1 k_1)\Omega_1} \qquad A_1^3 = A_1^2 \frac{R_2 y_2 k_2 \Omega_1}{(R_3 - R_1)\frac{\partial \Omega_1}{\partial t} + (R_3 k_3 - R_1 k_1)\Omega_1}$$

$$A_2^3 = A_2^2 \frac{R_2 y_2 k_2 \Omega_2}{(R_3 - R_2)\frac{\partial \Omega_2}{\partial t} + (R_3 k_3 - R_2 k_2)\Omega_2} \qquad A_1^4 = A_1^3 \frac{R_3 y_3 k_3 \Omega_1}{(R_4 - R_1)\frac{\partial \Omega_1}{\partial t} + (R_4 k_4 - R_1 k_1)\Omega_1}$$

$$A_2^4 = A_2^3 \frac{R_3 y_3 k_3 \Omega_2}{(R_4 - R_2)\frac{\partial \Omega_2}{\partial t} + (R_4 k_4 - R_2 k_2)\Omega_2} \qquad A_3^4 = A_3^3 \frac{R_3 y_3 k_3 \Omega_3}{(R_4 - R_3)\frac{\partial \Omega_3}{\partial t} + (R_4 k_4 - R_3 k_3)\Omega_3}.$$

Since Ω_j and $\partial \Omega_j / \partial t$ have closed analytical formulae (13) and (16), respectively, the transform matrix $\mathbf{A}$ is exactly analytical and the concentration solutions are analytically described using (5). Though the analytical solution is not written in a single formula, the implementation of the solution scheme can be summarized as

$$\mathbf{\Omega} \longrightarrow \frac{d\Omega}{dt} \longrightarrow \mathbf{A} \longrightarrow \mathbf{c}. \tag{20}$$

5. Application and Analysis

5.1. Comparison with Lunn *et al.* [1996]

Lunn *et al.* [1996] developed analytical solution to a transport system of three species first-order decay chain. The model is written as

$$(1+K_d)\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial x^2} - v\frac{\partial c_1}{\partial x} - k_1' c_1$$

$$\frac{\partial c_2}{\partial t} = D\frac{\partial^2 c_2}{\partial x^2} - v\frac{\partial c_2}{\partial x} - k_2 c_2 + k_1' c_1$$

$$\frac{\partial c_3}{\partial t} = D\frac{\partial^2 c_3}{\partial x^2} - v\frac{\partial c_3}{\partial x} - k_3 c_3 + k_2 c_2 \tag{21}$$

where $k_1' = k_1(1+K_d)$ and K_d is constant adsorption coefficient. We used the same column geometry and defined system parameters as shown in Table 1.

Table 1. System parameters used in Lunn *et al.*'s [1996] model

Velocity	v	0.1	$cm\ h^{-1}$
Dispersion coefficient	D	0.18	$cm^2\ h^{-1}$
Retardation factor 1	$R_1 = 1 + K_d$	2	
Retardation factor 2	R_2	1	
Retardation factor 3	R_3	1	
1st-order reaction rate 1	k_1	0.025	h^{-1}
1st-order reaction rate 2	k_2	0.03	h^{-1}
1st-order reaction rate 3	k_3	0.02	h^{-1}

The initial and boundary conditions are assumed as

$$c_1(x,0) = c_2(x,0) = c_3(x,0) = 0$$

$$c_1(0,t) = 1.0 \quad c_2(0,t) = c_3(0,t) = 0. \tag{22}$$

Figure 1 demonstrates a good match between the solution derived by Lunn *et al.* [1996] and the new solution derived in this paper after 200 h. Although the new solution can be considered identical to Lunn *et al.*'s solution, the coding effort required is significantly reduced.

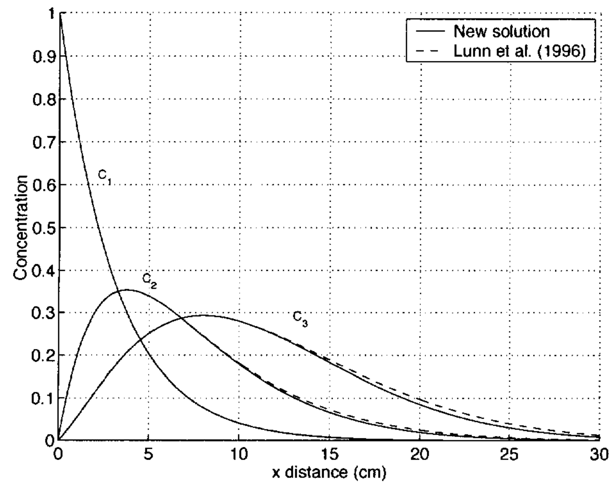

Figure 1. Concentration profiles of three species transport with a constant boundary condition. $t = 200\ h$, $R = (2,\ 1,\ 1)$, $k = (0.025,\ 0.03,\ 0.02)\ h^{-1}$, $c_0 = (1.0,\ 0.0,\ 0.0)$, $a = 1.8\ cm^2h^{-1}$, $v = 0.1\ cmh^{-1}$.

5.2. Comparison with Sun *et al.* [1999]

In order to demonstrate that the Sun *et al.* [1999] transform is a typical case in (10), we use a four-species transport problem in a one-dimensional column [Bear, 1979, p. 268] and assume $\mathbf{c}^o = [1,\ 0,\ 0,\ 0]$, $R_1 = R_2 = R_3 = R_4 = 1$. Using the Sun *et al.* [1999] transform, the solution of four species concentrations can be written

$$
\begin{aligned}
c_1 &= a_1 \\
c_2 &= a_2 - \frac{y_1 k_1}{k_1 - k_2} c_1 \\
c_3 &= a_3 - \frac{y_2 k_2}{k_2 - k_3} c_2 - \frac{y_1 y_2 k_1 k_2}{(k_1 - k_3)(k_2 - k_3)} c_1 \\
c_4 &= a_4 - \frac{y_3 k_3}{k_3 - k_4} c_3 - \frac{y_2 y_3 k_2 k_3}{(k_2 - k_4)(k_3 - k_4)} c_2 - \frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_4)(k_2 - k_4)(k_3 - k_4)} c_1
\end{aligned}
\tag{23}
$$

where

$$
\begin{aligned}
a_1 &= \Omega_1 \\
a_2 &= \frac{y_1 k_1}{k_1 - k_2} \Omega_2 \\
a_3 &= \frac{y_1 y_2 k_1 k_2}{(k_1 - k_3)(k_2 - k_3)} \Omega_3 \\
a_4 &= \frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_4)(k_2 - k_4)(k_3 - k_4)} \Omega_4.
\end{aligned}
\tag{24}
$$

Substituting $a_i, \forall i = 1, 2, 3, 4$ and the ancestor concentrations in the daughter species concentrations, the species concentrations can be expressed as linear functions of the basic solutions (4)

$$c_1 = \Omega_1$$

$$c_2 = -\frac{y_1 k_1}{k_1 - k_2}\Omega_1 + \frac{y_1 k_1}{k_1 - k_2}\Omega_2$$

$$c_3 = \frac{y_1 y_2 k_1 k_2}{(k_1 - k_2)(k_1 - k_3)}\Omega_1 - \frac{y_1 y_2 k_1 k_2}{(k_1 - k_2)(k_2 - k_3)}\Omega_2 + \frac{y_1 y_2 k_1 k_2}{(k_1 - k_3)(k_2 - k_3)}\Omega_3$$

$$\begin{aligned} c_4 = &-\frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_2)(k_1 - k_3)(k_1 - k_4)}\Omega_1 + \frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_2)(k_2 - k_3)(k_2 - k_4)}\Omega_2 \\ &- \frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_3)(k_2 - k_3)(k_3 - k_4)}\Omega_3 + \frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_4)(k_2 - k_4)(k_3 - k_4)}\Omega_4 \end{aligned} \tag{25}$$

where all components of the transform matrix are identical to those derived from (10).

$$A_1^1 = \mathbf{1}$$

$$A_1^2 = -\frac{y_1 k_1}{k_1 - k_2} = A_1^1 \frac{k_1}{k_2 - k_1}$$

$$A_2^2 = \frac{y_1 k_1}{k_1 - k_2} = 0 - \frac{y_1 k_1}{k_2 - k_1} = c_2^o - A_1^2$$

$$A_1^3 = \frac{y_1 y_2 k_1 k_2}{(k_1 - k_2)(k_1 - k_3)} = A_1^2 \frac{y_2 k_2}{k_3 - k_1}$$

$$A_2^3 = -\frac{y_1 y_2 k_1 k_2}{(k_1 - k_2)(k_2 - k_3)} = A_2^2 \frac{y_2 k_2}{k_3 - k_2}$$

$$A_3^3 = \frac{y_1 y_2 k_1 k_2}{(k_1 - k_3)(k_2 - k_3)} = 0 - \frac{y_1 y_2 k_1 k_2}{(k_1 - k_2)(k_1 - k_3)} + \frac{y_1 y_2 k_1 k_2}{(k_1 - k_2)(k_2 - k_3)} = c_3^o - A_1^3 - A_2^3$$

$$A_1^4 = -\frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_2)(k_1 - k_3)(k_1 - k_4)} = A_1^3 \frac{y_3 k_3}{k_4 - k_1}$$

$$A_2^4 = \frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_2)(k_2 - k_3)(k_2 - k_4)} = A_2^3 \frac{y_3 k_3}{k_4 - k_2}$$

$$A_3^4 = -\frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_3)(k_2 - k_3)(k_3 - k_4)} = A_3^3 \frac{y_3 k_3}{k_4 - k_3}$$

$$\begin{aligned} A_4^4 &= 0 + \frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_2)(k_1 - k_3)(k_1 - k_4)} - \frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_2)(k_2 - k_3)(k_2 - k_4)} + \frac{y_1 y_2 y_3 k_1 k_2 k_3}{(k_1 - k_3)(k_2 - k_3)(k_3 - k_4)} \\ &= c_4^o - A_1^4 - A_2^4 - A_3^4. \end{aligned} \tag{26}$$

5.3. Central line concentrations of a BIOCHLOR example

Aziz *et al.* [1999] implemented the Sun *et al.* [1999] solution for multiple first-order decay chains with the same retardation factor in the BIOCHLOR code. To understand what role retardation factors play in the sequentially reactive transport, we use the example of dechlorination in BIOCHLOR,

$$\underset{(PCE)}{c_1} \underset{y_1}{\xrightarrow{k_1}} \underset{(TCE)}{c_2} \underset{y_2}{\xrightarrow{k_2}} \underset{(DCE)}{c_3} \underset{y_3}{\xrightarrow{k_3}} \underset{(VC)}{c_4} \xrightarrow{k_4} \tag{27}$$

where PCE, TCE, DCE, and VC are tetrachloroethylene, trichloroethylene, dichloroethylene, vinyl chloride, respectively. When the system parameters are defined as in Table 2, the central line concentrations are shown in Figure 2. The solid line represents the new solution $c_i, \forall i = 1, 2, 3, 4$ when unique retardation factors $[7.1, 2.8, 2.9, 1.4]$ are used while the dashed line represents the central-line concentrations, $c'_i, \forall i = 1, 2, 3, 4$, calculated from BIOCHLOR, when the average retardation factor, $\bar{R} = 2.9$ is used for every species. Figure 3 shows the steady state concentrations of four species along the central line in the study domain of Domenico [1987]. Initially, c_4 advances slower than c'_4 (Figure 2), but after steady state is reached, it advances farther (Figure 3).

Table 2. Data set for BIOCHLOR example

Velocity	v	111.7	$ft\ yr^{-1}$
Dispersivity	a	40	ft
Retardation factor 1	R_1	7.1	
Retardation factor 2	R_2	2.9	
Retardation factor 3	R_3	2.8	
Retardation factor 4	R_4	1.4	
1st-order reaction rate 1	k_1	2.0	yr^{-1}
1st-order reaction rate 2	k_2	1.0	yr^{-1}
1st-order reaction rate 3	k_3	0.7	yr^{-1}
1st-order reaction rate 4	k_4	0.4	yr^{-1}
Boundary concentration 1	c_1^o	56.00	$mg\ L^{-1}$
Boundary concentration 2	c_2^o	15.80	$mg\ L^{-1}$
Boundary concentration 3	c_3^o	98.50	$mg\ L^{-1}$
Boundary concentration 4	c_4^o	3.08	$mg\ L^{-1}$
Yield coefficient 1→2	y_1	0.79	
Yield coefficient 2→3	y_2	0.74	
Yield coefficient 3→4	y_3	0.64	
Time	t	1.5	yr

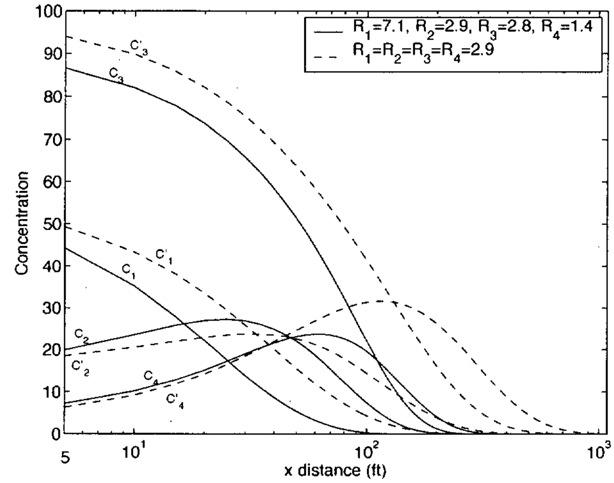

Figure 2. Concentration c_i profiles of four species transport calculated using our new solution scheme are compared with central-line concentrations c_i' calculated from BIOCHLOR.

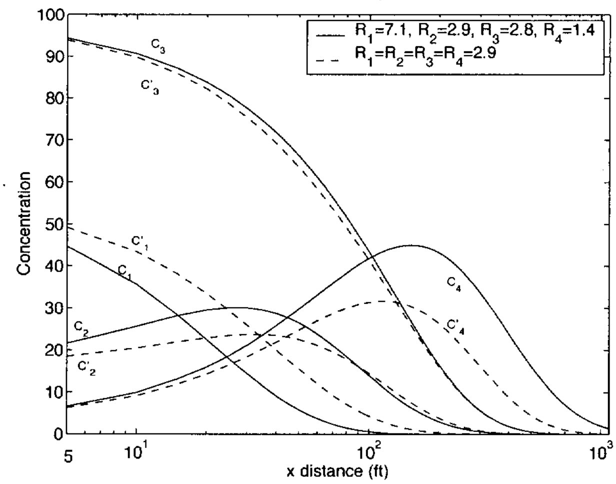

Figure 3. Steady state concentration profiles of four species transport calculated in the study domain of Domenico [1987] are compared to those calculated using our new solution scheme.

5.4. Extension to Domenico's domain

Domenico [1987] derived an analytical solution of a single species with first-order decay in three dimensions. Aziz *et al.* [1999] implemented this solution with the Sun *et al.* [1999] transform in the BIOCHLOR code. To overcome the restriction of the same retardation factor, here we apply the recursive transform with Domenico's [1987] solution, which can be expressed as the product of lateral distribution factor and longitudinal concentration distribution [Petersen and Sun, 2000]

$$c(x, y, z) = c^o \gamma(x, y, z) \Omega'(k) = c^o \Omega(k), \tag{28}$$

where

$$\gamma(x,y,z) = \frac{1}{4}\left\{\mathbf{erf}\frac{y+Y/2}{2(a_y x)^{1/2}} - \mathbf{erf}\frac{y-Y/2}{2(a_y x)^{1/2}}\right\}\left\{\mathbf{erf}\frac{z+Z/2}{2(a_z x)^{1/2}} - \mathbf{erf}\frac{z-Z/2}{2(a_z x)^{1/2}}\right\} \tag{29}$$

and $\gamma(0,0,0) = 1$. Y and Z are the source dimensions $[L]$, and a_x, a_y, a_z are, respectively, longitudinal, transverse, and vertical dispersivities $[L]$. Since the lateral distribution factor γ is a function of spatial variables and dispersivities, it is species independent. Note that Ω' here is equivalent to Ω in (13) in the one-dimensional system. The basic solution for species i in three-dimensional Domenico's domain is redefined as

$$\Omega_i = \frac{\gamma}{2}\mathbf{exp}(\alpha_i x)\mathbf{erfc}(\beta_i) \quad \forall i = 1, 2, \cdots, n. \tag{30}$$

Correspondingly, the first derivative of Ω is

$$\frac{\partial \Omega_i}{\partial t} = \frac{\gamma}{4\sqrt{D_i \pi}}\mathbf{exp}\left(\alpha_i x - \beta_i^2\right)\left[\frac{x}{t^{3/2}} + \sqrt{\frac{v_i^2 + 4k_i D_i}{t}}\right] \quad \forall i = 1, 2, \cdots, n. \tag{31}$$

Using the same system parameters in Table 2, the concentration profiles of four species, when $t = 15\ yr$ and $z = 0$, are shown in Figure 4. Additional parameters are given as $a_x = 40$, $a_y = 10$, $a_z = 10$. Figure 4 also shows the comparison of concentration profiles (left column) derived from the new solution scheme and those (right column) calculated from BIOCHLOR.

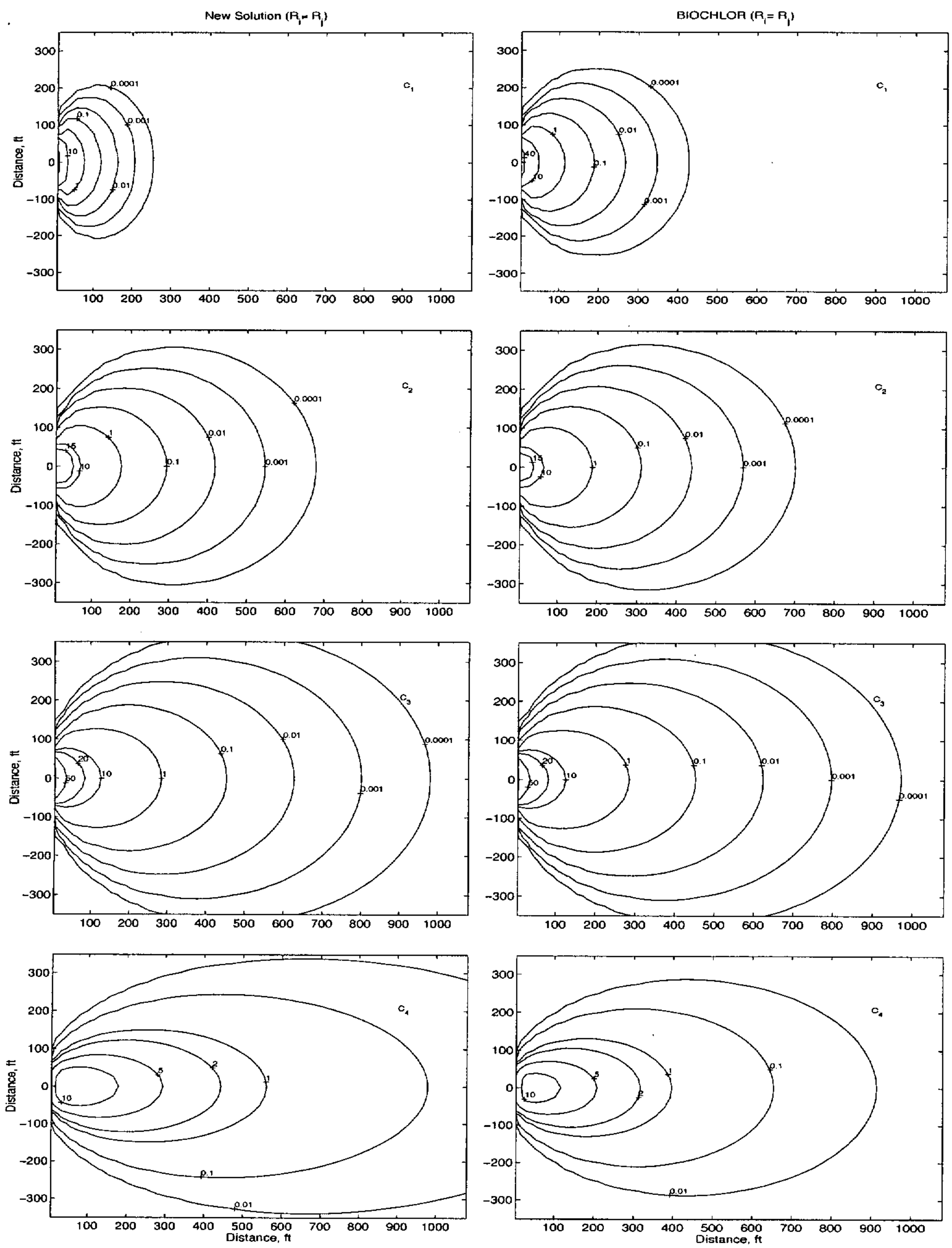

Figure 4. Concentration profiles of four species transport in Domenico's domain. Four contour plots in the left column are derived from the new solution scheme, $R = [7.1, 2.9, 2.8, 1.4]$, and four plots in the right column are calculated from BIOCHLOR, $\bar{R} = 2.9$.

5.5. Sensitivity Analysis

The effect of linear sorption on the mass transport of a single species has been extensively studied [Bear, 1979], To estimate the effect of retardation factors of parent species on the daughter species and understand the behavior of the sequentially reactive transport systems with different retardation factors, a sensitivity analysis is conducted using Lunn *et al.*'s [1996] model and the new solution. By changing R_1, R_2, R_3, respectively, and fixing all other system parameters, the concentration profiles of the end product are shown in Figure 5. The thick solid line represents the base case when $R_1 = 2$, $R_2 = 1$, $R_3 = 1$ as shown in Figure 1. Higher values of R_1 (grandparent), R_2 (parent), and R_3 (itself) make the transport of c_3 slower, but higher values of R_1 and R_2 make the concentration higher upstream and lower downstream while the higher value of R_3 makes the concentration of c_3 lower anywhere.

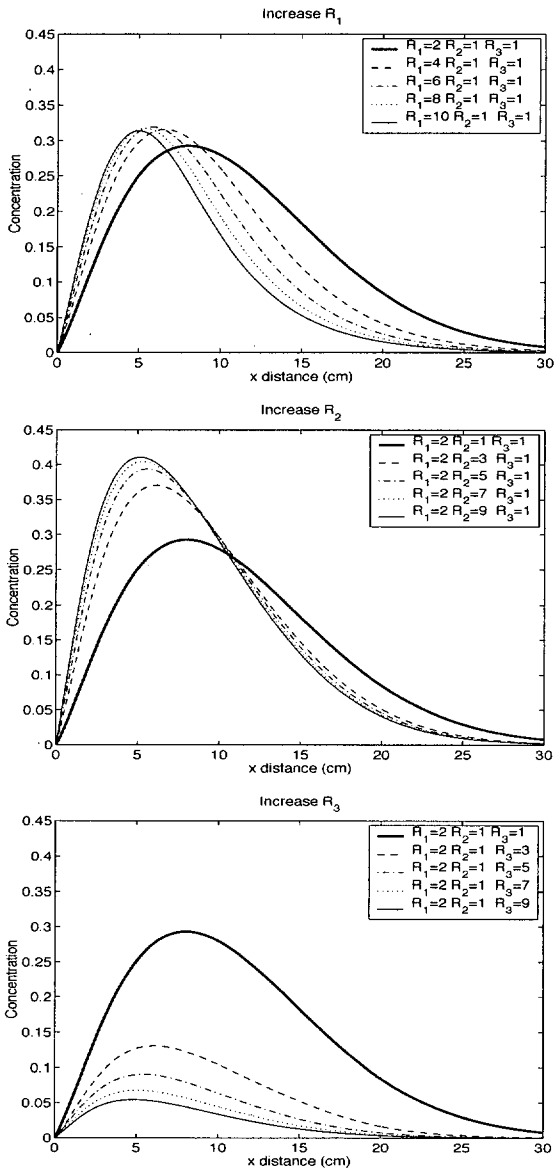

Figure 5. Concentration profiles of species 3 in Lunn *et al.*s' [1996] model after 200 h.

6. Conclusions

A solution scheme has been developed in the time domain for deriving analytical solutions of sequentially reactive transport systems with different retardation factors. To avoid the difficulty inherent in using inverse Laplace transforms, previously published analytical solutions for a single transporting species in the time domain are used as fundamental solutions. Since the partial differential equations are linear in species concentrations, a daughter species concentration can be expressed as a linear function of those fundamental solutions. The solution scheme accounts for stoichiometric yield coefficients. One unit of parent species unnecessarily produces one unit of daughter species. It has been demonstrated that Sun *et al.* [1999] transform with the same retardation assumption is a typical scenario in the recursive transform presented in this paper. The new solution derived using the solution scheme matches Lunn *et al.* [1996] for three species transport in a one-dimensional column.

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